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(54) PATTERNS IN RELIEF ON COATED SHEETS

(71) We, DANTANI SANGYO KABUSHIKI KAISHA, a Japanese corporation of No. 4-3 Higashiminato-machi, Kokuraku, Kitakyushu-shi, Fukuoka-ken, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —

The present invention relates to a method of forming a surface in relief on a sheet. The sheet may be a rigid or flexible material and may be of organic or inorganic material. For example the sheet, which is usually flat, may be of paper, cloth, synthetic resin, rubber, plywood, fibre board, particulate board, metal plate or foil, glass, porcelain or plaster board.

It is very desirable to be able to form a surface in relief on sheets in order that the surface can be made to have a three dimensional pattern resembling, for example, a natural grain pattern. In addition to being three dimensional the pattern is preferably also coloured.

The conventional means of forming surfaces in relief in sheets comprise embossing and engraved plate printing. Both of these require the use of an engraved plate or roll, and this involves high expense. Also the surface in relief that is obtained is rather unsatisfactory in that the three dimensional impression obtainable is rather poor and cracks and other defects are liable to occur. It is also known to form a pattern by a method known as " imitation embossing". In this printing is conducted with a plateless engraving ink, powder of a fusible resin is scattered over the printed surface and stuck to the ink while it is still incompletely dried and the adhering resin is heated and fused to the surface. However this method also does not give a very satisfactory three dimensional effect.

According to the invention we apply over a sheet a coating of a hardenable resinous material and before or after this application we print onto the sheet a printing ink in the positive or negative of the desired relief and subsequently harden the coating, and in this process the ink and the coating contain one or more ingredients such that the coating foams most or only in the desired depressed areas of the relief surface and, after hardening, we subject the coating to abrasion to form the desired surface in relief.

The pattern that is to be printed can be formed by photographic methods, and thus the ink to be printed can be applied by photogravure printing. Accordingly a very accurate reproduction is obtainable. An essential feature of the invention is that use is made of the fact that a hardenable material is more easily abraded if it is foamed than if it is unfoamed and that the ease of abrasion in any particular place depends upon the degree of foaming in that particular place. Accordingly by utilising the printed ink to control the degree of foaming and then abrading the product after foaming and hardening of the coating one can obtain an accurate three dimensional reproduction of the desired image.

Any convenient way of arranging that foaming occurs preferentially in the parts that are to be depressed can be used. The preferred method is to include in the printing ink a foaming agent and to rely upon this causing foaming of the coating in the printed areas. Foaming may advantageously be brought about as a result of reaction between the printing ink and a component in the coating, and most conveniently this component that reacts with the foaming agent is the hardening agent for the resin in the coating. However in another method the coating may contain the foaming agent and the printing ink may contain a material that promotes or inhibits reaction of the foaming agent with the result that, provided conditions for foaming are subsequently controlled appropriately, foaming will occur preferentially either in the printed or non-printed areas. In another method the coating may contain one reactant and the printing ink a second reactant neither of which are foaming

[*Price 33p*]

agents but which react together to form a compound which decomposes to cause foaming.

Combinations of foaming agents and inhibitors or accelerators and of reactants that will react together to form foaming agents can readily be found by experiment but examples will be seen in U.S. Patent Specifications Nos. 3,293,094 and 3,093,108 and in British Patent Specification No. 1,273,684.

It is generally preferred to print the printing ink and then to apply the coating of resin over the printed surface. Further, as already stated, it is preferred that the printing ink should contain a foaming agent and that the resin should contain a hardening agent which reacts with the foaming agent to cause foaming. It is also preferred that the coating of resin should be transparent since then the printing ink, in addition to causing the formation of a three dimensional effect, can also be used to form a coloured pattern if it is itself of a different colour from the sheet.

It has been found that the amino alkyl resins are very suitable for use as the coating and that they should preferably be of the acid setting type, preferably being hardenable at normal temperatures. Such resins are conventionally used for pre-finishing wood, especially plywood.

Amino alkyd resins usable in the invention are the initial condensates between nitrogen compounds, for example urea and/or melamine, and formaldehyde, or amino resins etherified with, for example, butanol, for instance butylated melamine resins, butylated benzo guanamine resins or butylated urea resins, or blends of such resins with others such as hexamethoxy methylolmelamine resins and alkyd resins. Preferably the alkyd resins used are short oil resins i.e. having an oil length of less than 44%, compatible with the amino resins, for example alkyd resins in which the mole ratio of glycerine: phthalic anhydride: fatty acid is 6:6:2 and the oil length is 31.5% or less. The weight proportion of amino resin to alkyd resin is preferably from 60:40 to 80:20. By oil length we mean the weight percentage of fatty acid based on the structural units of the resin.

The hardening agent is preferably an inorganic acid such as hydrochloric acid, sulphuric acid and phosphoric acid, or an acidic organic compound such as paranitrobenzenesulphonic acid or other sulphonates or butyl phosphate.

Suitable foaming agents which will be caused to decompose upon reaction with acidic hardening agents and thereby cause foaming include inorganic compounds such as calcium sulphide, iron sulphide, barium carbonate, alkali metal bicarbonate and organic bases such as dinitro-pentamethylene-tetramine (DPT).

In the preferred method of the invention a suitable pattern is printed on the surface of the sheet using a printing ink containing the foaming agent. The printing ink may be formulated in known manner and will be chosen having regard to the surface that is being printed. Thus if the surface is paper a printing ink for paper will be chosen. Likewise the ink may be a direct printing ink or a printing ink for metal. Printing inks for paper generally contain a solution of cellulose esters such as cellulose acetate and nitrocellulose as a vehicle, the ink for direct printing generally contains an alkyd resin solution as the vehicle, and the printing ink for metal generally contains mainly a vinyl resin solution as the vehicle.

Any convenient solvents may be used for forming the vehicle. One example is a solvent mixture comprising, in parts by volume, 60 parts methylethyl ketone, 30 parts methylisobutyl ketone and 10 parts acetone.

The following are typical examples of suitable printing ink formulations (in parts by weight).

Formula No.	1	2	3	4	5	6	7	8
Resin:								
Cellulose ester	–	–	–	–	50	50	–	–
Alkyd resin	50	50	50	50	–	–	10	
Vinyl resin	–	–	–	–	–	–	–	10
Pigment	30	30	35	30	30	30	30	30
Solvent	50	50	50	45	50	50	50	40
Foaming agent:								
Calcium sulphide	40	–	–					
Iron sulphide	–	35	–					
Barium carbonate	–	–	40					
Sodium bicarbonate	–	–	–	40				
D P T	–	–	–	–	35	30	40	40

When the sheet that is to carry the coating is a panel it may be convenient, instead of printing direct onto the surface of panel, to print onto paper and then to adhere the paper to the panel before applying the subsequent coating.

The hardenable resin is applied as a continuous coating over the surface as a solution in an appropriate solvent and may contain other additives, such as colouring materials and deglossing agents. Any desired colouring material, of any desired colour, may be used and generally well known pigments and dyes are suitable. Finely divided silica is suitable as a deglossing agent.

Any solvent for the resin may be used and typical solvents are alcohols such as ethanol and methanol, hydrocarbons such as toluene and xylene, and mixed solvents of alcohol and hydrocarbon. For example, a mixed solvent of alcohol and hydrocarbon at the ratio of 40—20 parts by volume of alcohol and 60—80 parts by volume of hydrocarbon is often found to be very satisfactory.

Advantageously the hardening agent is compounded into the coating material by dissolving the acid, for example both inorganic acid and organic acid substance, in a solvent of the alcohol series, e.g. ethanol, and then compounding the solution with the coating material.

By way of example, a hardening agent of the following composition may be used:

Hydrochloric, Sulphuric or Phosphoric acid	10 to 20 parts by volume
p-Nitrobenzene sulphonic acid or Butyl phosphate	10 to 20 parts by volume
Ethanol or Methanol	70 parts by volume

A preferred composition of the coating material is as follows:

Amino-alkyd resin	50 to 60 parts by weight
Solvent (Acetone, Methylethylketone, Xylene and/or Toluene)	34 to 80 parts by weight
Pigment (Green Gold)	any suitable amount
Deglossing agent (Silica, Talc or Kaolin)	0 to 60 parts by weight

These two compositions may then be mixed in the following proportion:

Resinous solution	100 parts by weight
Hardening agent solution	10 to 40 parts by weight

The compounded coating material may optionally be diluted with a diluent, and then used. The diluent may be the same as the solvent.

The invention is preferably carried out by printing the desired pattern, such as a grain pattern, on the base material by, for example, photogravure printing. Single colour or multicolour printing may be used. After drying the coating material is applied over the entire surface by conventional method, for example spray or roll coating. The hardening agent thereupon reacts with the foaming agent in the printed ink and thus in the printed areas the coating is raised and becomes porous. The coated product is usually carried through a drier whereupon the coated layer becomes dried and the resin hardens.

After hardening of the coating the surface is subjected to abrasion by, for example, a buffing roll sander, a paper sander or a brush roll. Naturally the abrading surface must be sufficiently resilient to effect abrasion of the foamed material even below the surface level of the unfoamed material.

The thickness of the coated layer will be chosen having regard to the desired pattern and the other process conditions but generally is from 30 to 60 grams per square meter.

As every part of the printed pattern will have a different amount of ink every part of the coated layer will give a different porosity, depending upon the amount of ink located under it in the preferred method. Accordingly the breaking strength of the raised portions will differ at different parts and so the raised portions are accordingly removed in an amount corresponding to the amount of ink underneath them. Thus concave portions corresponding to the grain or other printed pattern are formed and differ in depth and in shade and lustre at various parts in accordance with the desired pattern. Thus a dressed surface exhibiting a three dimensional impression closely resembling the natural grain or other pattern is obtained.

The resultant surface in relief can be used without further treatment. However it is often desirable to apply a transparent final finish coating over it. For this coating an amino alkyd resin may be used although another suitable coating material is, for example, a polyester resin. A typical composition comprises (using the hardening agent composition and coating material exemplified above):

Alkyd-amino resin solution	100 parts by weight
Hardener solution	10 parts by weight
Solvent or diluent	5 to 10 parts by weight

The invention is illustrated in the following drawings in which Figure 1 is a sectional view showing state in which a finish coating material is applied to cause drawn line parts to protrude in porous condition, Figure 2 is a sectional view showing a state in which the porous protrusions are removed by a sander, and Figure 3 is a sectional view showing a state in which a final finish coating material is further applied thereon. Figure 4 is a plan view showing an example of a panel manufactured by the method of the invention.

In the drawings, a plywood base plate 1 has a sheet 3 of paper with printing 2 thereon adhered to it. A coated layer 4 of hardenable material has been applied and as shown in Figure 1 at A it is foamed and protrudes along the lines of the printed pattern. After abrading the foamed parts are recessed, as shown in Figure 2. The bottoms of the resultant concave portions are composed of a number of convex parts α and concave parts B, which are respectively different in lustre and the concentrations of colour. As shown in Figure 3 a final finish coating layer 5 may then be applied.

The following are some examples of the invention.

Example 1.

A printing ink was prepared having Formula 6 above, wherein the cellulose ester is cellulose acetate and the solvent is a mixture of 60 parts by weight methylethyl ketone, 30 parts by weight methylisobutyl ketone and 10 parts by weight acetone. The ink was printed onto a sheet of paper and the printed paper adhered onto a plywood panel using an adhesive comprising a vinyl acetate resin emulsion, the paper and the panel being hot-pressed together in a hot press or in a laminating machine.

A primary coating composition was then prepared comprising 100 parts by weight of a 60% solids amino alkyd resin solution, and 40 parts by weight of a hardening agent solu-

tion that consisted of 20 parts by weight 20 to 30% hydrochloric acid, 15 parts by weight butyl phosphate and 65 parts by weight ethanol.

This transparent material was applied to the printed paper on the plywood to a thickness of 6 to 8 g/900 cm² using a roll coater. The layer was dried for 10 minutes in a drier through which hot air was circulated at 100 to 120°C, the film thus becoming hardened. The coated surface was then subjected to abrasion using buffing rolls of #240, #320 and #400, to remove foamed projections. A final finish coating was then applied comprising 100 parts by weight of resin solution, 10 parts by weight hardening agent solution and 10 parts by weight of a diluent mixture of 30 parts ethanol and 70 parts toluol, the hardening agent and resin solutions being the same as used for the initial coating above. The final coating was then dried by the hot air circulating drier.

Example 2.

A printing ink of Formula 7 above wherein the solvent mixture is 40 parts toluol and 60 parts xylol was formulated and was printed by photogravure offset printing onto a plywood surface which had been filled and coloured with foundation colour. An initial coating of the same composition as described in Example 1 was then applied to a thickness of 6g/900 cm² by means of a roll coater and was then dried, abraded and recoated (using the same final finish coating composition) and dried as described in Example 1.

Example 3.

A printing ink of Formula 8 above wherein the solvent is a mixture of 70 parts by weight methylethyl ketone and 30 parts by weight acetone was printed onto an aluminium foil which was then bonded onto a plywood panel using an emulsion of a modified vinyl acetate resin.

An initial coating of the same composition as described in Example 1 was then applied onto the aluminium foil surface by a sprayer to a thickness of 6g/900 cm². The coating was then dried, abraded, further coated and dried as in Example 1.

Example 4.

The process of Example 1 was repeated except that the printing ink had a composition according to Formula 1 above, as the primary coating composition there was used a mixture of 100 parts by weight of a 57% solids melamine resin solution and 30 parts by weight hardening agent solution while as the finish coating composition there was used a mixture of 100 parts by weight of the 57% solids melamine resin solution, 10 parts by weight hardening agent solution and 10 parts by weight of a diluent consisting of 30 parts by weight ethanol and 70 parts by weight toluol. In each of these coating compositions the hardening agent solution consisted of 20 parts by weight 20 to 30% hydrochloric acid, 70 parts by weight ethanol and 10 parts by weight *p*-nitrobenzene-sulphonic acid.

WHAT WE CLAIM IS:—

1. A process for forming a surface in relief on a sheet comprising applying a coating of hardenable resinous material over the sheet and before or after this application printing onto the sheet a printing ink in the positive or negative of the desired relief and subsequently hardening the coating, in which process the ink and the coating contain one or more ingredients such that the coating foams most or only in the desired depressed areas of the relief surface and in which, after hardening, the coating is subjected to abrasion to form the desired surface in relief.

2. A process according to claim 1 in which a transparent coating is applied over the abraded surface.

3. A process according to either preceding claim in which the sheet is a panel.

4. A process according to claim 1 or claim 2 in which the sheet is a sheet of paper which is printed and adhered to a panel before the coating of hardenable resinous material is applied over it and before subjecting the coating to abrasion.

5. A process according to any preceding claim in which the printing ink contains a foaming agent which foams upon reaction with a hardening agent that is included in the coating of hardenable resinous material.

6. A process according to claim 5 in which the hardenable resin is an acid setting amino alkyd resin.

7. A process according to claim 6 in which the hardening agent is selected from hydrochloric acid, sulphuric acid, phosphoric acid, paranitrobenzene sulphonic acid and butyl phosphate.

8. A process according to any of claims 5 to 7 in which the foaming agent is selected from calcium sulphide, iron sulphide, barium carbonate, alkali metal bicarbonate and dinitro-pentamethylenetetramine.

9. A process according to any of claims 5 to 8 in which the sheet is printed with the ink and the hardenable resin is applied subsequently and forms a transparent coating.

10. A process according to claim 1 substantially as herein described with reference to any of the Examples.

11. A sheet having a surface in relief formed by a process according to any preceding claim.

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1383024 COMPLETE SPECIFICATION
2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*
Sheet 1

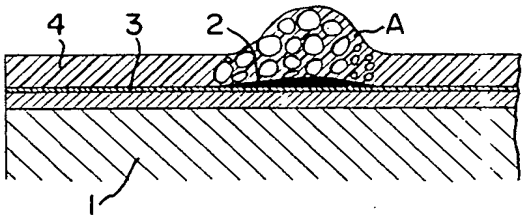

FIG.1

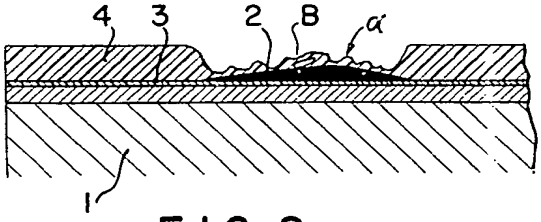

FIG.2

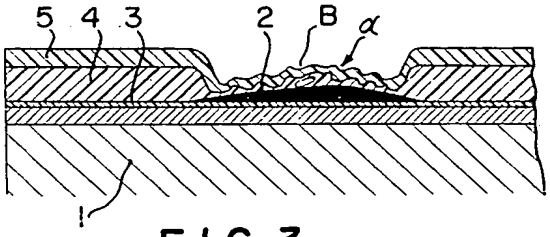

FIG.3

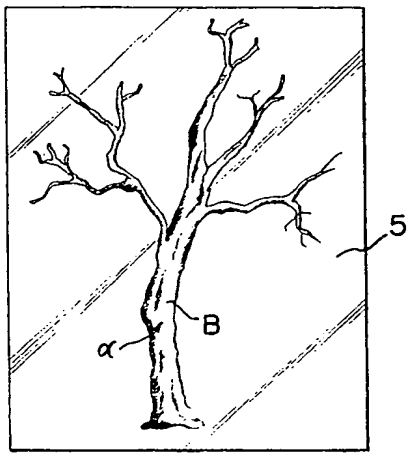

FIG.4